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A METHOD FOR DETERMINING THE CHANGE IN TRANSFERENCE NUMBER OF A SALT WITH CHANGE IN CONCENTRATION. A MODIFICATION OF THE MOVING BOUNDARY METHOD

By Edgar Reynolds Smith

ABSTRACT

A method for determining the rate of change of the transference number of a salt with change in concentration, based on a modification of the moving boundary method, is described. Junctions between solutions of the same salt at different concentrations are formed and the volumes through which the junctions move during the passage of known amounts of electricity are measured. The changes in transference numbers between the concentrations across the junctions are calculated from these data. The method was tested for solutions of lithium, sodium, and potassium chloride. It was found that potassium chloride exhibits but little change in transference number on passing from dilute to 4.7 molal solution.

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I. NOTATION

C, concentration in moles per cubic centimeter.
M, concentration in moles per 1,000 gs of water.
T_R, transference number of ion constituent R.
T'_R, dT_R/dC.
i, current density.
F, 96,500 coulombs.
t, time.
x, distance.
V, volume.
Q, $\int \frac{i}{F} dt$.
U, cation mobility.
W, anion mobility.
E, electrical potential.
l, specific conductance.

II. INTRODUCTION AND THEORY

When a current of electricity is passed through a solution of an electrolyte the concentration of which varies from point to point, there will, in general, be an accompanying shift in the concentration at

every point, due to the well-established fact that ion mobilities are functions of the concentration. In what follows, the flow of electricity is considered to be unidirectional through a cylindrical tube of constant cross section having electrodes so far removed from the portion under consideration that changes in concentration resulting from the electrode reactions do not enter that portion. Also the effects of diffusion are neglected, or rather eliminated, since the prevention of diffusion by the action of the electric current is one of the necessary conditions for the measurement of transference numbers by the moving boundary method. The general equations governing concentration shifts during electrolysis were developed some time ago by Kohlrausch.[1] For the simple case of a single uniunivalent electrolyte, C^+A^-, in aqueous solution the desired equations may be obtained as follows:

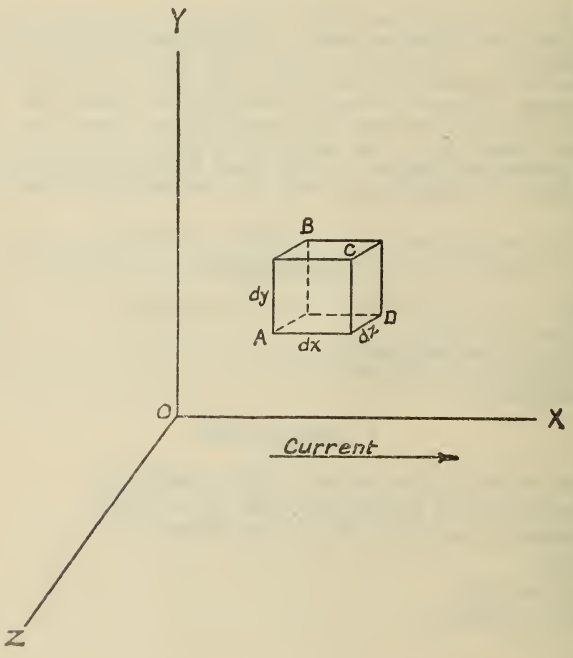

FIGURE 1.—*Element of volume*

Consider an element of volume $dv = dx\ dy\ dz$ in the solution. (Fig. 1.) The number of cations entering the face AB in the time dt is

$$N_{AB} = U\frac{dE}{dx}C\ dy\ dz\ dt = \frac{i}{F}T_c\ dy\ dz\ dt$$

Since

$$dE/dx = i/l = i/CF(U+W)$$

and

$$U/(U+W) = T_c$$

[1] F. W. Kohlrausch, Ann. Physik, 62, p. 209; 1897.

while the number of cations leaving the element through the face CD is

$$N_{CD}=\frac{i}{F}T_c\,dy\,dz\,dt+\frac{i}{F}\frac{\partial T_c}{\partial x}\,dx\,dy\,dz\,dt$$

The rate of increase in concentration is therefore

$$\frac{\partial C}{\partial t}=-\frac{i}{F}\frac{\partial T_c}{\partial C}\frac{\partial C}{\partial x}\text{ or }\frac{\partial C}{\partial Q}+T'_c\frac{\partial C}{\partial x}=0 \qquad (1)$$

since

$$\partial C/\partial t=(N_{AB}-N_{CD})/(dx\,dy\,dz\,dt)$$

The integral of equation (1) in terms of an arbitrary function ϕ is

$$C=\phi\ (x-T'_cQ) \qquad (2)$$

as can be shown by differentiation of this integral to obtain equation (1). Initially the concentration is a known function of the position; that is, $C=\psi\ (x)$ when $Q=0$, a condition which determines the nature of the function ϕ. Therefore equation (2) becomes

$$C=\psi\ (x-T'_cQ) \qquad (3)$$

A junction between two solutions of the same salt at two different concentrations C_1 and C_2 can be considered as a region of continuous, even if rapid, change in concentration between C_1 and C_2. Observations on the motion of such a junction will, therefore, give information on the nature of T' between the two concentrations.

The stability of boundaries of this type is probably connected with the space charge resulting from the variation in potential gradient across the junction. From Poisson's equation, $-d^2E/dx^2=4\pi\sigma/D$ where σ is the space density of electric charge and D is the dielectric constant, it is clear that such a space charge must exist at the junction, forming an electric double layer which tends to preserve the discontinuity between the two solutions. When the current is reversed the sign of the double layer also reverses and the junction remains stable for either direction of the current. The following cases are of interest:

1. The transference number of the salt is constant. In this case $T'=0$, and the concentration everywhere retains its initial value of $\psi\ (x)$. As many ions of each kind must enter the junction from one side as leave it from the other and the junction remains stationary.

2. The transference number is a linear function of the concentration. In this case $T=a+kC$ and $T'=k=$constant. Then $C=\psi\ (x-kQ)$. The junction moves with a velocity of $k\cdot i/F$ as can be seen from equation (1). Therefore, a measurement of the velocity of the junction under the influence of a known current density will give dT/dC for the electrolyte.

3. The variation of transference number with the concentration is nonlinear. $T=f(C)$, $C=\psi\{x-f'(C)\cdot Q\}$, and at each instant the concentration condition at any point moves with a velocity of $if'(C)/F$. The usual type of this variation is illustrated in Figure 2 for lithium chloride and sodium chloride, the data being taken from

International Critical Tables.[2] It is seen from the figure that T' is negative and a junction between any two concentrations should remain sharp and travel in a direction opposite to the direction of the current. A simple equation for calculating the transference number in such a case can easily be derived by reference to Figure 3. Let ΔV = the volume through which the junction moves when Q equivalents of electricity are passed and ΔN = the increase in number of equivalents of salt in the volume ΔV accompanying the passage of the electricity. Suppose the junction moves down the tube while

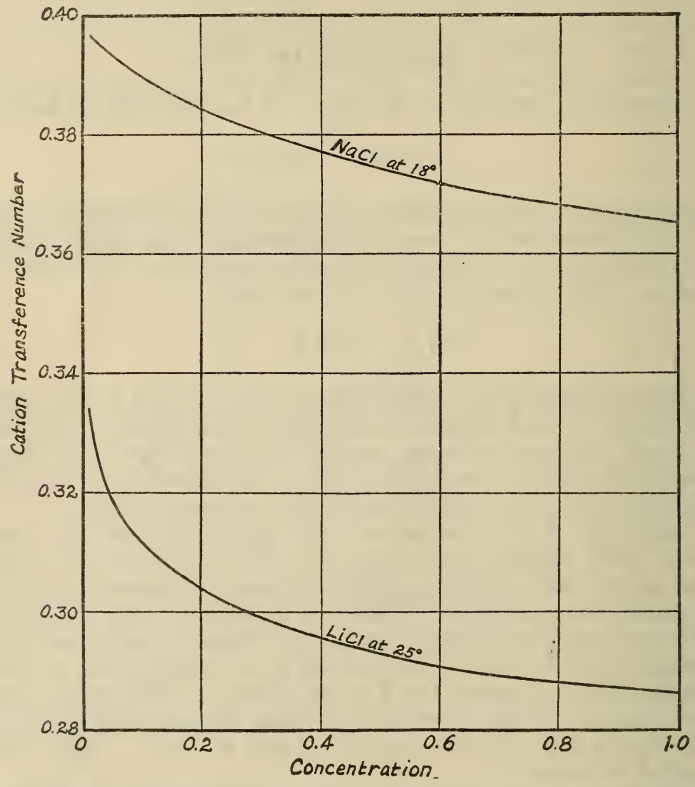

FIGURE 2.—*Transference numbers of lithium and sodium chlorides*

the current moves up through the solutions. Then $\Delta N = \Delta V(C_1 - C_2)$ and $\Delta N = \Delta N_C = \Delta N_A$ for electric neutrality. Therefore, $\Delta N_C = \Delta V \cdot (C_1 - C_2)$. Also $\Delta N_C = Q(T_1 - T_2)$. Solving for $(T_1 - T_2)$ gives

$$(T_1 - T_2) = \frac{\Delta V(C_1 - C_2)}{Q} \text{ or } \Delta T_c = \frac{\Delta V \cdot \Delta C}{Q} \tag{4}$$

If the transference number should happen to go through a maximum or a minimum value between the concentrations C_1 and C_2 on opposite sides of the junction, the motion becomes more complicated. For example, in Figure 4 at the left-hand limit of the junction

[2] Int. Crit. Tables, 6, p. 310, McGraw-Hill Co., New York; 1929.

where the concentration is C_1, $f'(C)$ is positive and the motion will be in the direction of the current, while at the right-hand limit where the concentration is C_2 and $f'(C)$ is negative the motion will be opposite to the direction of the current. thus, with the current flowing from C_1 to C_2, the junction tends to sharpen. Now, if the transference numbers T_1 and T_2 are nearly the same a slight adjustment in concentration by the action of the current might change the sign of the direction of motion of the junction by changing the sign of $\triangle T$ across the junction. Such an adjustment might take place if the current were stopped for a moment and then reversed. The junction, instead of reversing its motion with current reversal, might continue to move in the same direction as before.

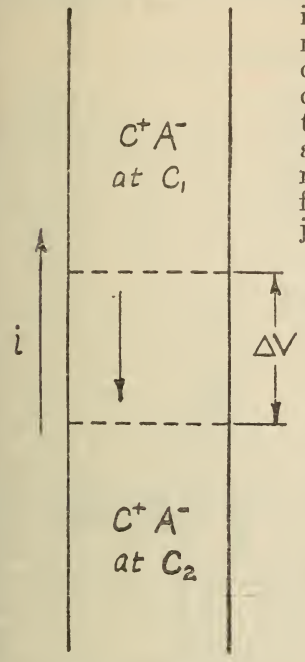

FIGURE 3.—*Moving junction between two salts*

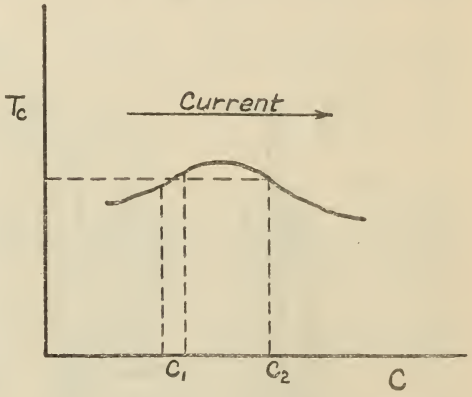

FIGURE 4.—*Variation of transference number with concentration*

III. APPARATUS AND MANIPULATION

The transference cell is shown in Figure 5. The anode consisted of a piece of platinum gauze rolled into a cylinder and coated electrolytically with silver. The cathode was prepared in the same way, but with an additional coating of silver chloride and was immersed in precipitated silver chloride. The reservoir G was used in filling the right-hand side of the apparatus with the more concentrated solution, including the junction tube T, which had an inside diameter of approximately 0.4 cm. The electrode tube A and the tube H were filled with the less concentrated solution. The method of separating the solutions at the start by means of the plunger F has been described in another paper.[3] After the junction had been formed, with the current flowing, it was pulled down the tube T to any suitable reading point on the scale S. This operation was carried out by opening stopcocks D and C while E was closed thus withdrawing solution from the left-hand side. For this purpose the tube I, partly capillary

[3] E. R. Smith, J. Am. Chem. Soc., 50, p. 1904; 1928.

at the open end and carrying the stopcock *C*, extended over the front side of the thermostat. When the junction had reached a suitable position, stopcock *D* was shut, thus making the right-hand side of the apparatus tightly closed by ground-glass joints. The measuring tube *T* was calibrated with mercury for volumes compared with readings on the glass scale *S* which was attached to the tube at a fixed mark.

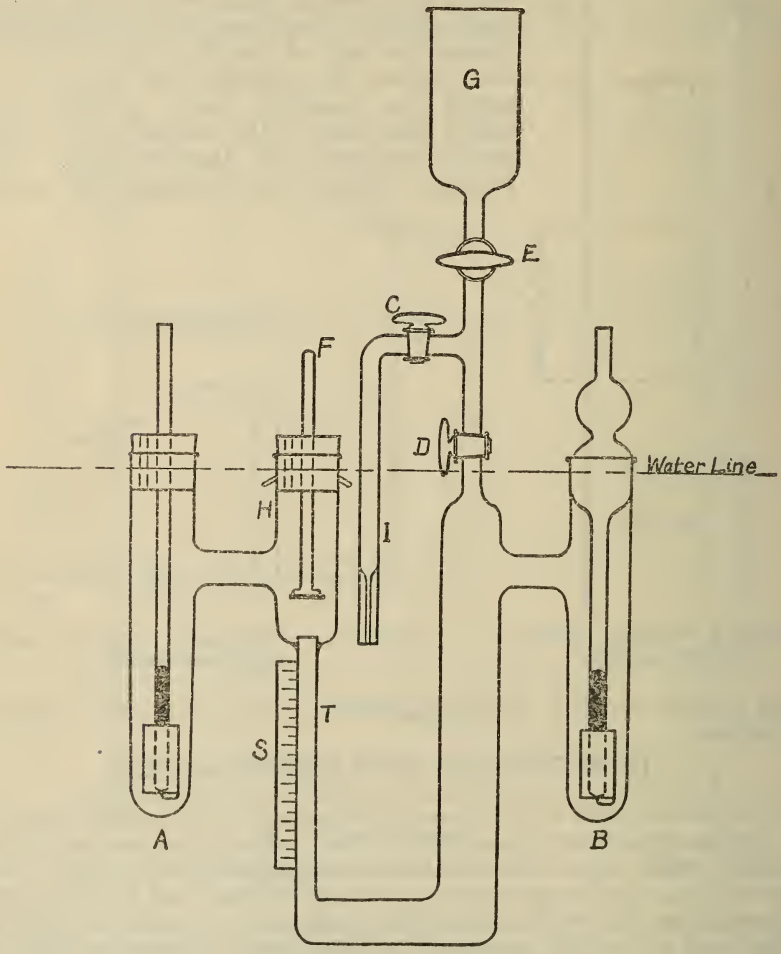

FIGURE 5.—*Transference cell*

The apparatus was immersed in a small water thermostat having plate glass front and back and provided with a stirrer, heater, and mercury contact regulator which held the temperature constant at 25° ± 0.05.

The quantities of electricity used were measured with a small copper coulometer consisting of a central cathode of heavy copper wire surrounded by a cylindrical sheet of copper in a beaker of 150 ml capacity. The order of magnitude of the cathode current density was 0.01 amp./cm.^{2}

The salts used were of "c. p." quality and were not tested or subjected to any further purification process. The solutions were prepared by weighing the proper quantities of salt and water to obtain the desired concentrations in terms of formula weights of salt per 1,000 g of water.

IV. EXPERIMENTAL RESULTS AND CONCLUSIONS

The object of the experimental work was to test the theory and conclusions given in Section II and to develop a rapid method for finding the direction and rate of variation of the transference number of a salt with change in concentration. For this purpose, lithium chloride with a rather rapid rate of change of transference number, sodium chloride with a moderate rate of change (fig. 3), and potassium chloride whose transference number is practically constant were chosen. It was also desired to determine if the constancy of the transference number of potassium chloride, which has been proved up to a concentration of 2 N[4], continues up to saturation. This knowledge would be of value in connection with the correction for or elimination of liquid junction potentials in cells containing a salt bridge of concentrated potassium chloride.

One experiment was made with lithium chloride, three with sodium chloride, and a larger number with potassium chloride. Correction for the change in volume due to the combination of electrode reaction and ion migration in the closed side of the cell was always applied. Because of the small volume of motion of the junction in this type of measurement the volume correction sometimes amounts to as much as 50 to 100 per cent of the measured volume. Usually the correction was from 10 to 30 per cent. All measurements were at 25° C. The data for the test with lithium chloride are shown in Table 1.

TABLE 1.—*Junction between lithium chloride solutions of concentrations 0.1 and 0.2 mole per 1,000 g of water*

Time (in minutes)	Cu deposited in coulometer	1/Q	Corrected volume of motion of junction	$C_1 \times 10^3$	$C_2 \times 10^3$
	g		*cc*		
80	0.0346	919	0.107	0.0995	0.1987

According to Figure 2, $dT_{Li}/dC = T'_{Li}$ is negative, and the theory requires that the junction move in the opposite direction to the direction of the current. This was found to be correct experimentally. From equation (4) and the data given in Table 1

$$\Delta T_{Li} = T_{Li}^{0.1} - T_{Li}^{0.2} = 0.107 \times 0.0992 \times 10^{-3} \times 919 = 0.00976 \qquad (5)$$

The values given in International Critical Tables, which are taken from the electromotive force measurements on lithium chloride concentration cells by MacInnes and Beattie[5] are $T_{Li}^{0.1} = 0.311$ and

[4] D. A. MacInnes (private communication).
[5] D. A. MacInnes and J. A. Beattie, J. Am. Chem. Soc., 42, p. 1117; 1920.

$T_{Li}^{0.2}=0.304$. If the latter is taken as a reference value and substituted in equation (5), the value obtained in this experiment for $T_{Li}^{0.1}$ will be $0.304+0.00976=0.314$ which is an approximate agreement. On reversing the current, the boundary reversed its direction of motion, and although the amount of electricity passed in the reverse direction was measured only roughly from the time and readings of a milliammeter, the agreement was equally satisfactory.

The data for the test with sodium chloride are given in Table 2. In each case with sodium chloride the junction moved in the predicted direction, against the current, reversed with reversal of current and afforded values of ΔT_{Na} in substantial agreement with the gravimetric values at 18°.

TABLE 2.—*Junctions between solutions of sodium chloride*

	Experiment No.		
	1	2	3
M_1	0.1	0.2	0.5
M_2	.2	.5	1
t (minutes)	68	45	40
Cu deposited in coulometer	.0415	.0409	.0400
1/Q	766	777	795
Corrected volume	.031	.027	.026
$C_1\times10^3$	.0995	.1987	.4941
$C_2\times10^3$	.1987	.4941	.9790
ΔT_{Na}	.0024	.0062	.010
ΔT_{Na} at 18° (Int. Crit. Tables)	.005	.011	.011

The experiments with potassium chloride can be divided into two groups. The first group, given in Table 3, was carried out with solutions in the concentration range of 0.05 to 1 molal where T_K is known to be practically constant. In these experiments the motion of the junction was in every case opposite to the direction of the current and reversed when the current was reversed. This would indicate a negative sign for dT_K/dC. However, the junction shifts were small, and the somewhat uncertain correction for the volume changes at the electrode amounted to a considerable fraction of the measured shift. In view of these facts the results are in excellent agreement with the known constancy of the transference number of potassium chloride in the measured range of concentration.

TABLE 3.—*Junctions between potassium chloride solutions having concentrations up to 1 molal*

	Experiment No.				
	1	2	3	4	5
M_1	0.05	0.1	0.2	0.4	0.2
M_2	.1	.2	.4	.7	1.0
$C_1\times10^3$	.04980	.09943	.1983	.3944	.1983
$C_2\times10^3$	.09943	.1983	.3944	.6844	.9093
t (minutes)	90	65	35	35	51
g Cu plated in coulometer	.0430	.0450	.0278	.0376	.0391
1/Q	739	706	1,143	845	813
Corrected volume (ml.)	.033	.019	.007	.001	.005
ΔT_K	.0012	.0013	.0016	.00025	.0031
$100\,\Delta T_K/T_K$ (per cent)	.25	.27	.32	.05	.63

TABLE 4.—*Junctions between potassium chloride solutions having concentrations of from 1.0 to 4.7 molal*

	Experiment No.				
	1	2	3	4	5
M_1	1.0	1.0	1.0	1.0	1.0
M_2	1.5	2.0	3.0	4.0	4.7
$C_1 \times 10^3$	.969	.969	.969	.969	.969
$C_2 \times 10^3$	1.433	1.883	2.742	3.551	4.088
t (minutes)	27	28	25	24	30
g Cu plated in coulometer	.0347	.0381	.0361	.0351	.0433
I/Q	916	834	880	906	734
Corrected volume (ml.)	.002	.005	.003	.002	.006
ΔT_K	.00085	.0038	.0047	.0046	.014
$100\Delta T_K/T_K$ (per cent)	.17	.78	.96	.94	2.8

The second group of experiments with potassium chloride was carried out with 1 N potassium chloride as the reference solution for the purpose of determining if the transference number remained practically constant from 1 N up to saturation. Table 4 contains the data for this group. In all these experiments with the more concentrated solutions the current was passed from the more concentrated to the 1 molal solution and the junctions shifted slightly in the direction of the current indicating a positive value for dT_K/dC. In experiment 1 the junction reversed its direction when the direction of the current was reversed, but in the others the following peculiarities were noticed. In experiments 2 and 4 the junction remained stationary when the current was passed in the reverse direction, indicating a constant transference number. In experiments 3 and 5 the junction continued at about the same rate without changing its direction when the current was reversed. These peculiarities are hard to explain quantitatively, but it is possible that in such concentrated solutions complex formations may be a disturbing factor causing the apparent transference number to pass through a slight maximum or minimum value, so that a small concentration adjustment on either side of the junction changes the sign of ΔT across the junction. This same phenomenon was encountered with a junction between 0.05 and 0.2 molal potassium chloride solutions, but was not observed between 0.05 and 0.1 or between 0.1 and 0.2 molal solutions. If the effect is due to a slight maximum or minimum it would be expected to disappear on changing one of the concentrations. However, the results indicate that there is but little change in the transferene number of potassium chloide in going from dilute to the saturated solution.

A more extensive study of the behavior of junctions of this type is planned, including an experimental determination of the actual volume changes occurring in the electrode portions. The results obtained in this investigation are to be considered as a preliminary survey to test the theory and practicability of such measurements.

V. ACKNOWLEDGMENT

The author desires to express appreciation to E. W. Washburn, chief chemist of this bureau, for many helpful suggestions and advice during the course of this work and to D. A. MacInnes and L. G. Longsworth, of the Rockefeller Institute for Medical Research, for valuable discussion and criticism.

Washington, March, 26, 1931.

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